

The worm-like chain model at small and large stretch

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The relation between force and stretch in the worm-like chain model of entropic elasticity is examined. Although no closed-form expression is valid for all values of forcing, solutions in the form of asymptotic series can be obtained under conditions of small and large applied force. The small and large stretch limits correspond to regular and boundary layer perturbation problems, respectively. The perturbation problems are solved and series solutions obtained for force as a function of stretch. The form of the asymptotic series suggest a uniform approximation valid for all stretch that is an improvement on existing approximations.

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I. INTRODUCTION

The worm-like chain (WLC) is a model of entropic elasticity [1] for a macromolecule under thermal agitation. The main feature of the model, as compared to simpler ones such as the freely jointed chain (FJC) model [2], is the inclusion of bending energy. Applications of the WLC model range from macroscopic elasticity of rubber and elastomers [3] to DNA unfolding [4]. With the increase in interest and application there is a need to more clearly understand how the WLC model relates mechanical parameters, and in particular, the relation between the force applied at the chain ends and the stretch. This is complicated by the implicit and complex functional dependence in the model.

The objective of this paper is to provide, for the first time, explicit analytical expressions for the applied force as a function of the stretch of the WLC. We begin with a brief introduction of the WLC model, and a review of existing closed-form approximations to the force-stretch relationship.

II. THE WORM-LIKE CHAIN MODEL

An excellent overview of the theory underlying the WLC model is given by Marko and Siggia [5]. Consider a uni-dimensional flexible chain of total length L_0 with end-to-end applied force \mathbf{F} . The free energy of the chain is

$$E_{WLC} = \int_0^{L_0} dl \left(\frac{L_p}{2\beta} |\mathbf{t}'|^2 - \mathbf{t} \cdot \mathbf{F} \right), \quad (1)$$

where L_p is the persistence length, $\mathbf{t}(l)$ is the unit tangent vector, and $\beta = (kT)^{-1}$. The applied force results in average stretch z at temperature T .

The natural non-dimensional units of force and stretch

are

$$f = \beta L_p F, \quad s = z/L_0. \quad (2)$$

Using standard arguments from statistical mechanics [5, 6]

$$s = \frac{L_p}{L_0} \frac{\partial \ln Z}{\partial f}, \quad (3)$$

where Z is the partition function over all possible states. It is certainly the case in elastomers, and generally true for DNA, that the persistence length is much less than the unfolded molecule end-to-end length. The large parameter $L_0/L_p \gg 1$ ensures that $\ln Z$, which can be identified as chain entropy, is dominated by the lowest energy state. As a result [5] $Z \approx -(L_0/L_p)\epsilon_0$, where ϵ_0 is a nondimensional energy, defined as

$$\epsilon_0 = \min_{\psi} \int_{-1}^1 dx \left[\frac{1}{2} (1-x^2)(\psi')^2 - f x \psi^2 \right]. \quad (4)$$

The probability density function is normalized $\langle \psi, \psi \rangle = 1$

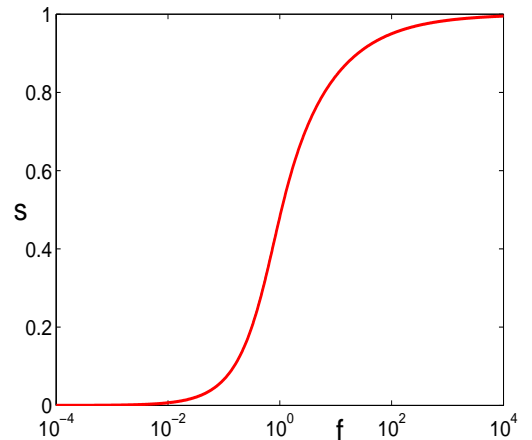


FIG. 1: The WLC relation between stretch s and applied force f . The numerical method is summarized in the Appendix.

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with respect to the inner product

$$\langle \psi, \phi \rangle = \int_{-1}^1 dx \psi(x) \phi(x). \quad (5)$$

The function ψ is smooth and bounded for all $-1 \leq x \leq 1$. The stretch is then

$$s = -\frac{\partial \epsilon_0}{\partial f} = \int_{-1}^1 dx x \psi^2. \quad (6)$$

The two terms in ϵ_0 of (4) correspond to the bending and work terms in the original energy E_{WLC} , and the specific form of the integrands is associated with rotational invariance about the force axis, with $\mathbf{t} \cdot \mathbf{F} = F \cos \theta = Fx$.

The WLC problem therefore requires finding stationary values of the functional

$$\begin{aligned} \Gamma(\psi) = & \int_{-1}^1 dx \frac{1}{2} (1 - x^2) (\psi')^2 - f \left(\int_{-1}^1 dx x \psi^2 - s \right) \\ & - \epsilon_0 \left(\int_{-1}^1 dx \psi^2 - 1 \right). \end{aligned} \quad (7)$$

$\Gamma(\psi)$ contains the bending energy term plus two constraints involving the first two moments of the function ψ . The normalization $\langle \psi, \psi \rangle = 1$ defines ψ as a probability density function, while the constraint (6)₂ defines the stretch s . We may consider the stretch as given, so that f and ϵ_0 are Lagrange multipliers, and the Euler-Lagrange equation is

$$\frac{1}{2} [(1 - x^2) \psi']' + f x \psi + \epsilon_0 \psi = 0, \quad -1 \leq x \leq 1, \quad (8)$$

The objective is to find the lowest value of ϵ_0 , and the force f is then uniquely determined as a function of s . This dictates an indirect procedure: consider f as given, and find ϵ_0 , the lowest eigenvalue of the differential operator that depends upon f . Then s is determined as a function of f via either formulas given by eq. (6). Note that the value of Γ at the minimum is $\gamma_0 = \epsilon_0 + s f$, which is the Legendre transform of ϵ_0 with $f = \partial \gamma_0 / \partial s$. The 2D version of eq. (8) reduces to the Mathieu differential equation with solution in terms of Mathieu functions [7]. Prasad et al. [7] derived small and large force limits for the WLC in two dimensions using this approach. The focus here is on the 3D problem only.

Figure 1 shows the characteristic WLC curve, obtained from eqs. (6) and (8) using a numerical method based on [5], see the Appendix. There are other ways to find $f = f(s)$, e.g. by solving the ODE using a shooting method [6]. The important issue is not, however, the numerical determination of the curve, but finding a suitable analytic approximation. An excellent first step in this direction was made by Marko-Siggia [5] who showed the leading order behavior for $f \ll 1$ and for $f \gg 1$ is $f = \frac{3}{2}s$ and $f^{-1} = 4(1 - s)^2$, respectively. Motivated by this limiting behavior they suggested the approximate functional form

$$f_{MS} = \frac{1}{4(1 - s)^2} - \frac{1}{4} + s. \quad (9)$$

This simple formula reproduces the small and large stretch leading order response in the respective limits. Ogden et al. [8] examined several alternative approximations based on intelligent curve fitting to the $f - s$ data in [6]. The simplest formula, which they called WLC_3 , is just the Marko-Siggia approximation with a single term added:

$$WLC_3 = \frac{1}{4(1 - s)^2} - \frac{1}{4} + s - \frac{3}{4}s^2. \quad (10)$$

The extra quadratic term $-\frac{3}{4}s^2$ produces a dramatic improvement, see Fig. 2. The root mean square error of WLC_3 is 0.013 as compared with 0.339 for f_{MS} . The analytical results of this paper will help explain this roughly 25-fold increases in accuracy. We will return to consider WLC_3 in Section V after deriving the small and large stretch approximations. The principal results of the papers are summarized next.

A. Summary of the main results

The small and large stretch expansions are

$$f = \begin{cases} \frac{3}{2}s + \frac{33}{20}s^3 + \frac{3393}{1400}s^5 + \dots, \\ \frac{1}{4(1 - s)^2} + \frac{1}{32} + \frac{3}{64}(1 - s) + \frac{2559}{32768}(1 - s)^2 + \dots, \end{cases} \quad (11)$$

valid for $s \ll 1$ and $1 - s \ll 1$, respectively. Based on these limiting forms, and some numerical experimentation, we find that the following approximation to f shows significant improvement on WLC_3 ,

$$WLC_6 = \frac{1}{4(1 - s)^2} - \frac{1}{4} + s - \frac{3}{4}s^2 + \frac{1}{64}s^3(3 - 5s)(19 - 20s). \quad (12)$$

This has rms error of 0.0047 and is compared with WLC_3 in Fig. 2.

The remainder of the paper is organized as follows. The asymptotic series of eq. (11) are derived in Sections III and IV. The small stretch regime is considered first in Section III, where the solution is developed using regular perturbation methods. Large stretch is examined in Section IV. Although the problem is a singular perturbation, it is reduced to a regular perturbation expansion using an inner scaled variable. The two asymptotic series are compared with the exact solution in Section V. The new and improved approximate formula valid for all values of stretch, large and small, is proposed after some numerical experimentation.

III. SMALL STRETCH EXPANSION

A. Perturbation theory

Under small stretch, or equivalently small applied force, the WLC equation reduces to a regular pertur-

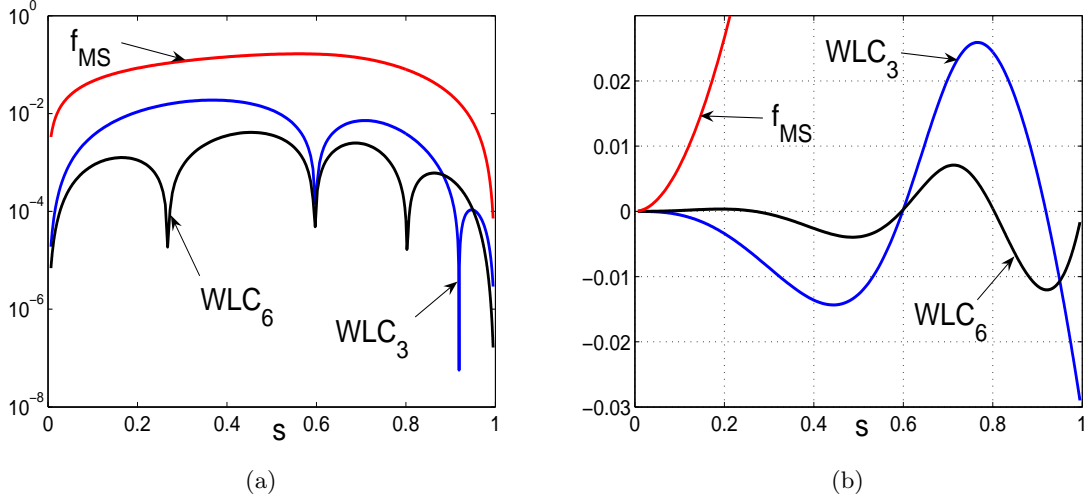


FIG. 2: The approximants f_{MS} , WLC_3 and WLC_6 of eqs. (9), (10) and (12) compared. The curves show the relative error compared with the exact solution on a log scale (a) and absolute value (b).

bation problem. Define

$$L = \frac{d}{dx}(1-x^2)\frac{d}{dx}, \quad (13)$$

then with the replacements $\epsilon_0 \rightarrow \frac{1}{2}\lambda$ and $f \rightarrow \frac{1}{2}\epsilon$ the equation (8) becomes

$$L\psi + \lambda\psi + \epsilon x\psi = 0, \quad -1 \leq x \leq 1. \quad (14)$$

The small stretch limit corresponds to $\epsilon \ll 1$. We seek solutions to eq. (14) in the form of a regular perturbation expansion

$$\psi = \psi_0 + \epsilon\psi_1 + \epsilon^2\psi_2 + \dots, \quad (15a)$$

$$\lambda = \lambda_0 + \epsilon\lambda_1 + \epsilon^2\lambda_2 + \dots \quad (15b)$$

Substituting these into eq. (14) and identifying terms of like order in the perturbation parameter ϵ yields a sequence of equations. The first few of order ϵ^0 , ϵ^1 and ϵ^2 , are respectively,

$$L_0\psi_0 = 0, \quad (16a)$$

$$L_0\psi_1 + x\psi_0 + \lambda_1\psi_0 = 0, \quad (16b)$$

$$L_0\psi_2 + x\psi_1 + \lambda_1\psi_1 + \lambda_2\psi_0 = 0. \quad (16c)$$

where

$$L_0 \equiv L + \lambda_0. \quad (17)$$

Although the WLC corresponds to $\lambda_0 = 0$, it is useful to first consider the perturbation of an arbitrary ground state.

The form of the $O(\epsilon^k)$, $k \geq 1$, equation is

$$L_0\psi_k + x\psi_{k-1} + \lambda_1\psi_{k-1} + \lambda_2\psi_{k-2} + \dots + \lambda_k\psi_0 = 0. \quad (18)$$

The unperturbed solution $\psi_0(x)$ is either an even or an odd function of x . It follows that ψ_k has the same or

opposite parity depending as k is even or odd, respectively. We assume the unperturbed solution is normalized $\langle\psi_0, \psi_0\rangle = 1$.

The operator L_0 is self adjoint with respect to the inner product (5), implying the solvability condition at $O(\epsilon^k)$ is

$$\lambda_k + \lambda_{k-1}\langle\psi_1, \psi_0\rangle + \dots + \lambda_1\langle\psi_{k-1}, \psi_0\rangle + \langle x\psi_{k-1}, \psi_0\rangle = 0.$$

The solvability condition essentially ensures that the solution to eq. (18) can be expressed in terms of a sum of Legendre polynomials that are regular at the end points, i.e. P_n . However, the expression for ψ_k has no component corresponding to ψ_0 , in other words, $\langle\psi_k, \psi_0\rangle = \delta_{k0}$. Taking into account the parity of the successive terms gives the succinct result

$$\lambda_{2k-1} = 0, \quad \lambda_{2k} = -\langle\psi_{2k-1}, \psi_0\rangle, \quad k = 1, 2, \dots \quad (19)$$

Note that the first few equations simplify to

$$L_0\psi_0 = 0, \quad (20a)$$

$$L_0\psi_1 + x\psi_0 = 0, \quad (20b)$$

$$L_0\psi_2 + x\psi_1 + \lambda_2\psi_0 = 0, \quad (20c)$$

$$L_0\psi_3 + x\psi_2 + \lambda_2\psi_1 = 0, \quad (20d)$$

$$L_0\psi_4 + x\psi_3 + \lambda_2\psi_2 + \lambda_4\psi_0 = 0, \quad (20e)$$

$$L_0\psi_5 + x\psi_4 + \lambda_2\psi_3 + \lambda_4\psi_1 = 0. \quad (20f)$$

We will solve these for the WLC problem, which corresponds to the lowest eigenvalue. Before considering the WLC specifically, we note some properties of the eigenvalue perturbation that are valid for any eigenvalue.

B. λ_2 for any initial state

The unperturbed eigenvalue problem is Legendre's equation, and hence the most general form of the un-

perturbed solution is

$$\psi_0(x) = c_n P_n(x), \quad \lambda_0 = n(n+1), \quad (21)$$

where P_n is the Legendre polynomial of order n and the normalization factor is $c_n = \sqrt{n + \frac{1}{2}}$.

Using the identity [9]

$$(2k+1)xP_k = kP_{k-1} + (k+1)P_{k+1}, \quad (22)$$

it is easy to show that

$$L_0(P_{k+1} - P_{k-1}(1 - \delta_{k0})) + 2(2k+1)xP_k = 0. \quad (23)$$

Hence, the first correction to the unperturbed mode is

$$\psi_1 = \frac{c_n}{2(2n+1)} (P_{n+1} - P_{n-1}(1 - \delta_{n0})). \quad (24)$$

The first correction to the eigenvalue follows from the identities [9]

$$\langle xP_l, P_n \rangle = \begin{cases} \frac{2n}{(2n-1)(2n+1)}, & l = n-1, \\ \frac{2(n+1)}{(2n+1)(2n+3)}, & l = n+1, \end{cases} \quad (25)$$

as

$$\lambda_2 = [2(2n-1)(2n+3)]^{-1}. \quad (26)$$

Note that $\lambda_2 > 0$ for all n except $n = 0$, which has the lowest eigenvalue. We now consider the lowest energy state specifically and continue the perturbation expansion to higher orders.

C. The lowest eigenvalue

We focus on the unperturbed solution for $n = 0$, which has the lowest initial energy. The analysis of the previous subsection gives the first two terms in the eigenvalue and eigenfunction expansions as $\lambda_0 = 0$, $\lambda_2 = -\frac{1}{6}$, and $\psi_0 = c_0 P_0$, $\psi_1 = \frac{c_0}{2} P_1$, with $c_0 = 1/\sqrt{2}$. These are the solutions of the first two in the hierarchy of equations (20). The next two are then solved to obtain ψ_2 and ψ_3 , from which the next term in the eigenvalue expansion, λ_4 , follows from eq. (19).

In this manner the first six equations given in (20) may be solved successively. The terms in the eigenfunction expansion were obtained using Mathematica,

$$\psi_0 = c_0 P_0, \quad \psi_1 = \frac{1}{2} c_0 P_1, \quad \psi_2 = \frac{c_0}{18} P_2, \quad (27a)$$

$$\psi_3 = \frac{c_0}{3.4.5.6} (P_3 - 11P_1), \quad (27b)$$

$$\psi_4 = \frac{c_0}{7.8.9.10} (\frac{2}{5} P_4 - \frac{215}{9} P_2), \quad (27c)$$

$$\psi_5 = \frac{c_0}{273452} (\frac{8}{21} P_5 - \frac{212}{3} P_3 + \frac{7520}{7} P_1), \quad (27d)$$

and the corresponding expansion of the eigenvalue is

$$\lambda = -\frac{1}{6}\epsilon^2 + \frac{11}{1080}\epsilon^4 - \frac{47}{34020}\epsilon^6 + O(\epsilon^8). \quad (28)$$

The procedure can be continued; however the coefficients quickly become more unsightly.

D. Small stretch expansion

Taking into account the factor of 1/2 difference between eq. (14) and the WLC equation (8), the above analysis implies that the lowest perturbed energy is

$$\epsilon_0 = -\frac{1}{3}f^2 + \frac{11}{5.27}f^4 - \frac{8.47}{5.7.9.27}f^6 + \dots \quad (29)$$

The stretch follows from eq. (6),

$$s = \frac{2}{3}f - \frac{44}{5.27}f^3 + \frac{16.47}{5.7.9.9}f^5 + \dots, \quad (30)$$

and inverting the series gives

$$f = \frac{3}{2}s + \frac{33}{20}s^3 + \frac{9.13.29}{1400}s^5 + \dots \quad (31)$$

The accuracy of the small stretch expansion is shown in Fig. 3, with WLC_3 used as a comparison. The relative error of the three term asymptotic series is less than 10^{-3} for $0 \leq s < 0.3$, but the approximation deteriorates at higher values, as expected.

IV. LARGE STRETCH: A BOUNDARY LAYER APPROXIMATION

A. A singular perturbation problem

The large stretch limit corresponds to large values of the applied force f in eq. (8). We therefore consider

$$\frac{1}{2}L\psi + \lambda\psi + \epsilon^{-2}x\psi = 0, \quad -1 \leq x \leq 1, \quad (32)$$

for $\epsilon \ll 1$. The second order differential operator L is defined in eq. (13), and the factor of 1/2 is introduced for convenience. Equation (32) defines a singular perturbation problem for $\psi(x)$, describing a boundary layer solution that is non-zero only near $x = 1$. In order to deduce this introduce the boundary layer variable

$$X = (1-x)\epsilon^{-1}. \quad (33)$$

Let $\Psi(X) = \psi(x)$, and define Λ by

$$\lambda = -\epsilon^{-2} + \epsilon^{-1}\Lambda, \quad (34)$$

then the equation for Ψ becomes

$$(X\Psi')' + (\Lambda - X)\Psi - (\epsilon/2)(X^2\Psi')' = 0, \quad (35)$$

for $0 \leq X \leq 2/\epsilon$. This is now a regular perturbation problem in terms of the rescaled inner coordinate X . Note that the range of X depends upon the small parameter ϵ , although this is not a serious complication since the effective range of X is the positive real axis.

Assuming the regular perturbation expansion

$$\Psi = \Psi_0 + \epsilon\Psi_1 + \epsilon^2\Psi_2 + \dots, \quad (36a)$$

$$\Lambda = \Lambda_0 + \epsilon\Lambda_1 + \epsilon^2\Lambda_2 + \dots, \quad (36b)$$

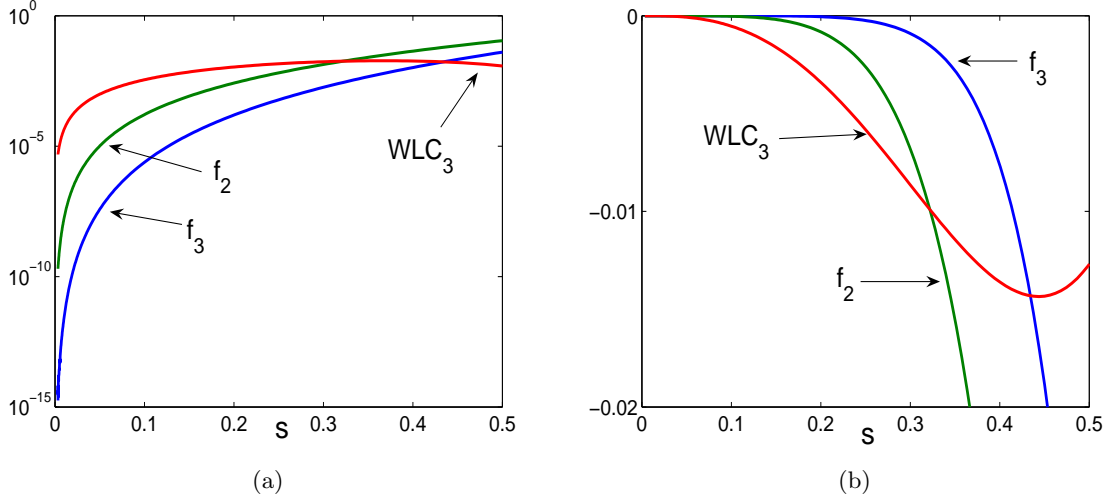


FIG. 3: The relative error of the perturbation solution compared with the exact solution at small stretch on a log scale (a) and absolute value (b). $f_3(s)$ is the three term expansion of eq. (31), and $f_2(s)$ is the first two terms only. The relative error of the WLC_3 approximation of eq. (10) is also shown.

gives the sequence of equations

$$(X\Psi'_0)' + (\Lambda_0 - X)\Psi_0 = 0, \quad (37a)$$

$$(X\Psi'_1)' + (\Lambda_0 - X)\Psi_1 + \Lambda_1\Psi_0 - \frac{1}{2}(X^2\Psi'_0)' = 0, \quad (37b)$$

etc. The solution of the first equation, of order ϵ^0 , is

$$\Psi_0(X) = C_0 e^{-X}, \quad \Lambda_0 = 1, \quad (38)$$

where normalization implies $C_0 = \sqrt{2}$. The next equation, of order ϵ^1 , becomes

$$(X\Psi'_1)' + (1 - X)\Psi_1 + (\Lambda_1 + X - \frac{1}{2}X^2)\Psi_0 = 0. \quad (39)$$

The solvability condition

$$\int_0^\infty dX (\Lambda_1 + X - \frac{1}{2}X^2)\Psi^2(X) = 0, \quad (40)$$

implies the first correction is $\Lambda_1 = -\frac{1}{4}$.

It is evident that the solutions have the form of the fundamental exponentially decaying solution $\Psi_0(X)$ multiplied by polynomials in X . This suggests scaling Ψ with respect to the leading order solution,

$$\Psi(X) = g(X)\Psi_0(X). \quad (41)$$

The equation for g is

$$Jg + \epsilon Hg + (\Lambda - 1 - \Lambda_1\epsilon)g = 0, \quad (42)$$

where the differential operators J and H are

$$Jg(X) = Xg'' + (1 - 2X)g', \quad (43a)$$

$$Hg(X) = (X - \frac{X^2}{2} - \frac{1}{4})g + (X^2 - X)g' - \frac{X^2}{2}g''. \quad (43b)$$

Assuming the expansion

$$g = g_0 + \epsilon g_1 + \epsilon^2 g_2 + \dots, \quad (44)$$

then $g_0 = 1$ and the equations for g_1 through g_4 are

$$Jg_1 + Hg_0 = 0, \quad (45a)$$

$$Jg_2 + Hg_1 + \Lambda_2 = 0, \quad (45b)$$

$$Jg_3 + Hg_2 + \Lambda_2 g_1 + \Lambda_3 = 0, \quad (45c)$$

$$Jg_4 + Hg_3 + \Lambda_2 g_2 + \Lambda_3 g_1 + \Lambda_4 = 0, \quad (45d)$$

The procedure is then to find g_1 as the particular solution to eq. (45a) and Λ_2 follows from the solvability condition for eq. (45b):

$$\int_0^\infty dX (\Lambda_2 + Hg_1)\Psi_0^2(X) = 0. \quad (46)$$

These steps are repeated to find the successive functions g_k and the eigenvalue coefficients Λ_k .

Equations (45) were solved using Mathematica. We omit the detailed form of the g_k functions and focus on the eigenvalue solution which is all that is required for the WLC model,

$$\lambda = -\frac{1}{\epsilon^2} + \frac{1}{\epsilon} - \frac{1}{4} - \frac{1}{64}\epsilon - \frac{3}{512}\epsilon^2 - \frac{885}{262144}\epsilon^3 + O(\epsilon^4). \quad (47)$$

B. Large stretch expansion

The boundary layer solution with $\epsilon = f^{-1/2}$ implies that the lowest energy state of the WLC has the large force expansion

$$\epsilon_0 = -f + f^{\frac{1}{2}} - \frac{1}{4} - \frac{1}{64f^{\frac{1}{2}}} - \frac{3}{512f} - \frac{885}{262144f^{\frac{3}{2}}} + \dots \quad (48)$$

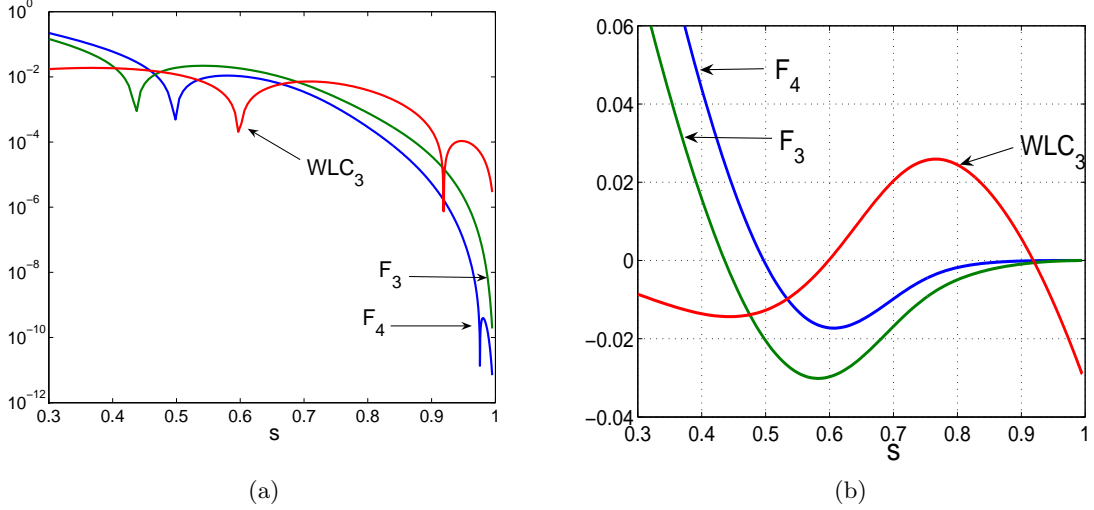


FIG. 4: The relative error of the perturbation solution compared with the exact solution at large stretch on a log scale (a) and absolute value (b). $F_4(s)$ is the four term expansion of eq. (50), and $F_3(s)$ is the first three terms only. The relative error of the WLC_3 approximation of eq. (10) is also shown.

The stretch is then

$$s = 1 - \frac{1}{2f^{\frac{1}{2}}} - \frac{1}{27f^{\frac{3}{2}}} - \frac{3}{29f^2} - \frac{5.9.59}{2^{19}f^{\frac{5}{2}}} + \dots \quad (49)$$

Inverting the asymptotic series gives the desired expression for f as a function of s ,

$$f = \frac{1}{4(1-s)^2} + \frac{1}{32} + \frac{3}{64}(1-s) + \frac{2559}{32768}(1-s)^2 + \dots \quad (50)$$

The large stretch asymptotic expansion is illustrated in Fig. 4, with WLC_3 again used as a comparison. The relative error of the four term series is less than 10^{-3} for $0.8 < s \leq 1$, roughly.

V. NUMERICAL EXPERIMENTS

Comparison of the accuracy of the small and large stretch expansions in Figs. 3 and 4 indicate the series as developed here are accurate to within on part in 10^3 for the range $0 \leq s < 0.3$ and $0.8 < s \leq 1$, with zero error at $s = 0$ and $s = 1$. This Section examines the question of finding an approximation that is uniformly valid over the entire range of stretch.

The difference between the exact force function and WLC_3 at small stretch follows from eqs. (10) and (11) as

$$f - WLC_3 = \begin{cases} \frac{s^3}{8} \left(\frac{26}{5} - 10s + \frac{1293}{175}s^2 \right) + O(s^6), \\ \frac{1}{32} - \frac{29}{64}(1-s) + \frac{27135}{32768}(1-s)^2 \\ + O((1-s)^3). \end{cases} \quad (51)$$

The term $-\frac{3}{4}s^2$ that distinguishes WLC_3 from the Marko-Siggia approximation (9) therefore exactly cancels the error in the latter at $O(s^2)$ in the small stretch limit.

The quadratic for large stretch has zeros at $s = 0.9191$ and $s = 0.5337$. The first zero, being close to $s = 1$ can be attributed as the cause of the zero of $f - WLC_3$ at $s \approx 0.9189$, see Fig. (2). The zeros of the quadratic in (51) for small stretch are complex. However, as Fig. (2) indicates $f - WLC_3$ has a second zero at $s \approx 0.5986$. This property of WLC_3 , that it is exact at $s \approx 0.6$ and $s \approx 0.92$, partly explains its success as a uniform approximant. This suggests that any attempt at improving on WLC_3 should maintain these zero crossings, and preferably increase the number of zero crossings.

At the same time wish to improve the accuracy at large stretch, requiring that the new approximation, say f^* , is exact at $s = 1$. Consider the two parameter extension $f^* = WLC_3 + cs^3(a-s)$, then the constraint $f^*(1) = 1/32$ implies $c = (a-1)/32$. Numerical experiments show that $f^* = WLC_3 + \frac{s^3(a-s)}{32(a-1)}$ is not an improvement on WLC_3 no matter what value of a is chosen. We therefore consider the two-parameter function

$$f^* = WLC_3 + \frac{s^3(a-s)(b-s)}{32(a-1)(b-1)}. \quad (52)$$

Using *fminsearch* in Matlab to minimize the root mean square error $\langle f - f^*, f - f^* \rangle^{1/2}$ gives $a = 0.5986$, $b = 0.9458$. Surprisingly, the value of a is precisely (to within four significant figures) the existing zero crossing of WLC_3 . In order to provide an approximation that is not too difficult to remember, we suggest rounding a and b up to 0.6 and 0.95, respectively. We call the resulting approximant WLC_6 ,

$$WLC_6 = \frac{1}{4(1-s)^2} - \frac{1}{4} + s - \frac{3}{4}s^2 + \frac{100}{64}s^3(0.6-s)(0.95-s). \quad (53)$$

The rms error incurred by WLC_6 is 0.0047, as compared with 0.0045 for f^* of (52) with $a = 0.5986$, $b = 0.9458$.

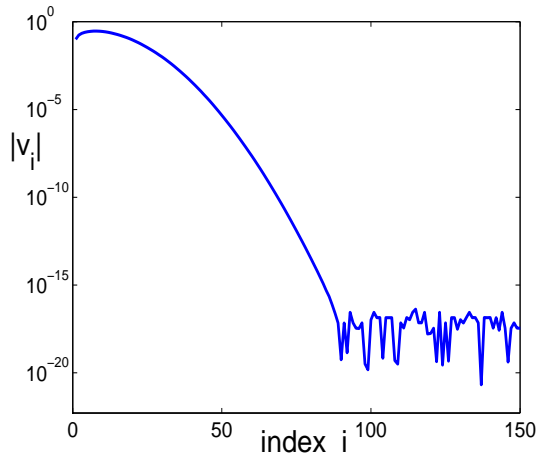


FIG. 5: The eigenvector components for $f = 10^4$ solved using Matlab with $N = 300$. Only the first 150 components are displayed, the rest are in the noise floor.

The rms errors for f_{MS} and WLC_3 are 0.3386 and 0.0132, respectively. These numbers indicate the remarkable accuracy of all three approximations to the exact force function $f(s)$.

APPENDIX A: EXACT SOLUTION

The exact solution for $s = s(f)$ can be determined numerically quite easily [5]. Define two symmetric matrices

of size $(N + 1) \times (N + 1)$ with elements

$$D_{ij} = \frac{i(i+1)}{2} \delta_{ij}, \quad S_{ij} = \frac{i\delta_{i-1,j} + j\delta_{i,j-1}}{\sqrt{(2i+1)(2j+1)}}, \quad (\text{A1})$$

for $i, j = 0, 1, 2, \dots, N$. Then for a given f , determine the minimum eigenvalue of $\mathbf{D} - f\mathbf{S}$ and its eigenvector \mathbf{v} . The strain is then

$$s = \mathbf{v}^t \mathbf{S} \mathbf{v} / (\mathbf{v}^t \mathbf{v}). \quad (\text{A2})$$

This algorithm can be effectively implemented in Matlab by using sparse matrix methods and the Matlab function *eigs* to find the single lowest eigenvalue. This is always negative but it is not always the smallest in magnitude, which is the criterion used in the function *eigs*. This can be circumvented by adding a multiple of the identity to $\mathbf{D} - f\mathbf{S}$ so that the lowest eigenvalue is also the smallest in magnitude, without the eigenvector unchanged. We find that $N=200$ is more than sufficient to find $s = s(f)$ for $f \leq 10^4$ with no apparent loss in numerical precision. Figure 5 shows the amplitudes of the eigenvector components for $f = 10^4$. Even at this large value the component with maximum amplitude is only v_6 .

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